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Exploratory Research on Novel Coal Liquefaction Concept
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CONTRACTOR NAME:
CONSOL Inc.
Research & Development
4000 Brownsville Road
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REPORTING PERIOD: October 1 through December 31, 1995

CONTRACT OBJECTIVES: No Change

SUMMARY OF TECHNICAL PROGRESS - OVERALL

Activities this quarter were conducted under Tasks 2 and 5. The Task 2 work was concentrated on evaluating the effects of first-stage reaction variables on coal conversion using the microautoclave, construction of a 1L reactor system for producing large quantities of first-stage reaction products, microfiltration tests with the first-stage products, and trial operation of the second-stage hydrotreater. Task 5 work was concentrated on the literature survey and defining the cost of production of the hydride ion reagent.

First-stage reaction (microautoclave) tests were conducted with Freedom Mine lignite and Black Thunder Mine subbituminous coal. For most tests, a single hydride ion source, "A" was used. The focus of this work was to define the effects of process variables on liquefaction performance. Variables tested include residence time, temperature, hydride ion reagent to coal ratio, water to hydride ion reagent ratio, and heating rate. Several tests also were made with an alternative hydride

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ion source, "B". Up to 91% conversion of coal to THF solubles (moisture and SO_3-free ash-free basis) was achieved with each coal. The results indicate that, at the temperature regime being tested, the hydride ion source is necessary for high coal conversions. Over the range of variables tested, coal conversion is sensitive to temperature, residence time, and hydride ion reagent to coal ratio, but less so to the other variables. Microautoclave test conditions and coal conversions are listed in Tables 1 and 2. The near-term direction of this work will be to evaluate the possible catalytic effect of sodium and to obtain complete material and elemental balances for tests at selected operating conditions. The latter results will used for the engineering and economic assessment.

The major elements of the one-liter first-stage reactor system were installed. Operation of the system to produce material for larger scale filtration tests will begin next quarter.

The microfiltration apparatus was designed, constructed, and operated. Microautoclave products for Freedom Mine lignite and Black Thunder Mine coal were filtered at 200 to 250 °C and the viscosities of the filtrates were measured. Filtration rates were high in all cases. Estimated specific cake resistivities indicate that acceptably fast filtration rates should be attainable. The solids contents of the filter cakes were determined to be 30 to 50%, depending on the filter feedstock. Larger scale filtration tests will be started next quarter as first-stage products from the 1L reactor become available.

Baseline and catalyst activation experiments were conducted using the second-stage microautoclave reactor system. The catalysts being tested are Molyvan L, Mo naphthenate, and presulfided AO60 supported catalyst. In the absence of first-stage product from hydride ion liquefaction, tests are being conducted with a Wilsonville deashed resid. Hydrotreating conditions are 400 to 440 °C, 60 min, and 2260 psia (hot) hydrogen partial pressure. At the higher temperature, resid conversions have been about 35%. Acceptable elemental balances were obtained. The activation step (375 °C, 30 min) had no major influence on resid conversion. Molyvan L was selected as the baseline catalyst. Future work will be directed toward selecting pretreatment conditions and finalizing the work-up and analytical schemes in preparation for operations with hydride ion liquefaction product.

The first edition and first update of the annotated bibliography of the review literature for this project were issued. LDP will prepare the next update of the annotated bibliography next quarter. A preliminary cost-of-production evaluation for a full-sized commercial plant for the production of hydride ion reagent "A" was completed.

SUMMARY OF TECHNICAL PROGRESS - BY TASK

Task 2 - Evaluation of Process Steps

Microautoclave Tests

Tests with Black Thunder coal and V1074 solvent, but no hydride ion reagent, at 350, 375, and 400 °C gave coal conversions 18 to 29 (average 24) absolute percentage points lower than runs at equivalent conditions but with the hydride ion reagent. Tests also were made with Black Thunder Mine coal at various hydride ion reagent to dry coal ratios at 350 °C. Coal conversion increased from 63 to 88 wt % as the ratio was increased seven-fold. The moisture content of this coal, about 20%, is insufficient to supply water (the ultimate source of hydrogen) in equimolar amounts to the hydride ion reagent in runs with high ratios of hydride ion reagent to coal. Therefore, tests were conducted with additional water added to the reaction system. At the conditions tested, the added water had little effect on coal conversion.

Microautoclave runs were made with the objective of finding conditions that give high coal conversion (≥90%) at low temperature (<400 °C), low hydride ion reagent to coal ratio (ca. 1), and moderate solvent to coal ratio (ca. 2). The approaches tried included increasing the residence time at temperature and reducing the heat-up rate. Both Freedom Mine lignite and Black Thunder Mine subbituminous coal were tested at the above conditions.

Extending the residence time at 350 °C and 375 °C improved coal conversions with both coals. With Freedom lignite at 350 °C, coal conversion increased from 59 to 80 wt % as residence time increased from 30 to 120 min. At 375 °C, coal conversion increased from 83 to 94 wt % as residence time increased from 45 to 150 min. With Black Thunder coal at 350 °C, conversion increased from 46% to 75% then remained at 75% as residence time was increased from 15 to 90 to 120 min. At 375 °C, coal conversion increased from 80 to 90 w t% as residence time was increased from 45 to 120 min.

Several experiments were conducted with Freedom Mine lignite using slow heating rates (4.5 °C/min and 2 °C/min), followed by various residence times at the final temperature of 350 °C. Coal conversions were essentially the same as those obtained in earlier tests at the same conditions but with the normal (fast) heating rate of 160 °C/min.

Several microautoclave runs were made with Black Thunder coal and an alternative hydride ion source that is not THF-soluble (reagent "B"). It was necessary to wash the THF-insoluble filter cake with water to determine coal conversion. Alternative hydride ion reagents will be further evaluated later.

A gas chromatograph was set up and calibrated with a multi-component calibration gas. Samples of gas from microautoclave runs are being analyzed.

A run plan was formulated to begin to investigate the possible catalytic effects of sodium content on coal conversion. Coteau Properties agreed to provide a sample of high-sodium lignite from the Freedom Mine.

Laboratory Support

Three sets of duplicate microautoclave tests were made by CONSOL with Black Thunder Mine coal to make material for CAER to use in their microfiltration studies. The samples were produced at conditions which give high, medium, and low coal conversion. Several of the 14 g samples were destroyed when they foamed out of their containers as CAER heated them to remove water and other light components. One of the samples was re-produced and shipped to CAER.

Two 800 g aliquots of Wilsonville 262E V1074 solvent were distilled to remove the 488 °C$^+$ fraction. The respective fractions from the two distillations were combined to provide ample solvent for upcoming tests. A 75 g aliquot of the distillate was sent to CAER.

One-Liter Autoclave

A site was prepared for installation of the 1 L autoclave and associated instrumentation. The reactor vessel was hydrostatically pressure tested and mounted. Electrical wiring was installed for the stirring motor, heaters and temperature controller. The temperature and pressure monitoring equipment were installed. A cooling coil was obtained for the reactor and cooling water lines were installed. Transfer lines were constructed between the 1 L autoclave and the 1 gal receiver. The cart designed to convey the one gallon collection vessel was fitted with the required hardware. The safety checklist and standard operating procedure were prepared for review.

Filtration

CAER designed and constructed a filtration rig capable of processing the small amount of first-stage reactor products (about 10g) from the CONSOL microautoclave tests. One of the objectives in the design and operation was to be able to minimize solids deposition on the filter membrane during heating of the test material to the filtration temperature. Three sets of duplicate samples produced at different reactor temperatures with lignite (representing coal conversions of 73, 84, and 92%) were heated in an air oven at a temperature of 135 °C to drive off residual amounts of light liquids. Weight loss was typically 2 to 3%. Filtration was performed at temperatures of nominally 200-250 °C and at pressure differentials of normally 30 psi. The overall rates of filtration were high in all cases.

Filtrates from duplicate runs were combined in order to provide enough sample to measure viscosities in the Brookfield thermocel unit. From these data, the viscosities at the filtration temperatures used were estimated (0.5-2 m-Pa). The specific cake resistivities then were calculated as around 10^{11} m/kg and under; such values are not unexpected for a non-softening coal (that is not to say that the values could have been predicted with great confidence). The THF-insoluble solids contents of these filter cakes were determined to be only around 30%, indicative of highly porous residual particles, again not unexpected for this feedstock. The micro technique (10 g and under) has worked well but, during this period, minor improvements to the equipment and its operating procedure were made.

The micro-filtration rig also was used to filter samples derived from Black Thunder coal. Intermediate storage of samples in smaller containers unfortunately proved counter-productive since the removal of light ends (<135 °C) prior to filtration caused excessive foaming, which in some cases caused sample loss. The filtration temperature was kept the same as for the lignite-based feedstock, i.e. 250 °C, but the pressure differential was reduced to 2.5 to 10 psig (cf 30 psig) in order to improve data collection by giving total filtration times in minutes rather than seconds. For the 400 °C produced feedstocks, the measured filter cake resistivities were around 5×10^{10} m/kg, which is similar to the lignite feedstocks; the solids contents of the filter cakes were higher at 40-50% (cf 30%) which would result in less subsequent processing. The first run with 375 °C feedstock indicated a cake resistivity about ten times higher, although this still could result in acceptably fast overall filtration rates. Further samples of Black Thunder-based feedstocks were received and their light ends were removed (without excessive foaming) in preparation for filtration.

Hydrotreating

CAER initiated catalyst activation experimental work using the microautoclave and the three candidate catalysts (AO60, Molyvan L, and Mo naphthenate) as described in the Project Management Plan. Standard cold gas charging pressures were selected which would yield $P_{H2\,hot}$ = 2260 psia, and 2 mol % H_2S (beginning with run R5-307-1). To determine resid conversions, duplicate 6-g samples of the raw deashed resid (Wilsonville Run 258A) selected for the catalyst presulfiding studies were distilled to a 1050 °F AET endpoint, and were found to comprise 75.7% ash-free resid. The ash content was determined to be 0.13%, compared with 0.10% reported by Wilsonville. To obtain baseline conversions without the use of an in situ activation step, three-gram samples of the deashed resid were reacted with the catalysts shown in Table 3 at 440 °C for 60 minutes, with reaction temperatures and pressures continuously recorded. The products were removed with THF and distilled.

The presulfided AO60 was prepared by grinding the extrudate to -100 mesh, drying in air at 250 °C for 8 hrs, and sulfiding for 4 hrs at 400 °C in 6 times the stoichiometric amount of H_2S required, using H_2S/H_2 sulfiding gas. It was subsequently stored under N_2. Samples of the sulfided catalyst were analyzed for S, Mo and Ni to verify that presulfiding was complete.

Additional runs were performed in which an in situ presulfiding step was included for each of the three catalyst precursors. For these runs the reaction mixture was held at 375 °C for 30 min prior to the hydrotreating stage at 440 °C for 60 min. The presulfiding step did not appear to significantly influence the resid conversion, Table 3. After this first round of testing, based on higher hydrogen consumption, Molyvan L was selected as the dispersed catalyst precursor to be mostly utilized for the balance of the study. Due to concerns that gas production was somewhat high for the hydrotreating runs conducted at 440 °C, a run was performed using 1000 ppm Molyvan L at 400 °C. Both gas yield and resid conversion were extremely low, and additional runs at this temperature have not been scheduled.

Elemental balances were performed for seven of the hydrotreating runs. Since gas constitutes a large percentage of the total mass of the reactants and the products for these experiments, it was found that accurate determinations of the initial and final gas volumes and compositions are essential for good balances. The average balances for the 7 runs were: C, 97.7%; H, 97.7%; and S, 95.6%. Balances on N and O were forced to 100% in order to obtain estimates for water and ammonia production. In general, the balances were considered acceptable for the conditions of these experiments. However, for runs in which a greater percentage of distillate materials are present, additional elemental balances will be performed.

The vendor for the high-temperature simulated distillation instrument (AC Analytical Controls, Bensalem, PA) was selected based on favorable test results with representative coal-liquid samples, and the unit was placed on order. Delivery is expected by the middle of the next quarter.

Task 5 - Engineering and Economic Study

The first edition and first update of the annotated bibliography of the review literature for this project were issued. Many of these references and additional articles dealing with the manufacture and utilization of hydride ion reagents were provided to LDP for review. LDP will prepare the next update of the annotated bibliography.

A preliminary cost-of-production evaluation for a full-sized commercial plant for the production of hydride ion reagent "A" was completed by LDP Associates. Contacts made with commercial manufacturers and literature sources tend to suggest that the preliminary estimate is reasonable for a large, dedicated plant. Integration of the plant with the conceptual hydride ion liquefaction plant approximately halves the production cost of reagent "A" by eliminating the feedstock costs.

Task 6 - Reporting

Bi-monthly conference calls were held, as scheduled, with UK/CAER and LDP. Reports documenting the calls were issued. The second quarterly review meeting was held on November 29 at CAER in Lexington, KY, and a meeting report was issued. The scheduled quarterly conference call with DOE was held on December 21. A conference record was issued.

TABLE 1

MICROAUTOCLAVE TEST CONDITIONS AND RESULTS
Freedom Mine, North Dakota Lignite

Run No.	Time, Min	Temp, °C	Hydride Ion Reagent	Solvent: dry coal g:g	HI:dry Coal g:g	HI:H_2O mole	Coal Conversion wt % MAF coal, SO_3-free Basis	Comments
3a	45	300	A	2.2	1.1	0.85	-	Reactor overfilled, sample lost
3b	45	300	A	2.3	1.1	0.83	19.7	524 °C⁻ product distilled from reactor before THF wash
2a	60	350	A	2.8	1.4	1.08	57.2	"
2c	60	350	A	2.2	1.1	0.85	66.1	"
2d	60	350	A	2.2	1.1	0.86	73.7	121 °C⁻ product distilled from reactor before THF wash
1	45	350	A	0.0	1.1	0.87	42.9	
2e	60	350	A	2.3	1.1	0.81	73.9	
11	45	400	A	2.2	1.1	0.85	92.0	
5	45	375	A	2.2	1.4	1.07	86.1	
13	60	350	A	2.3	1.1	0.82	68.1	Tetralin used as solvent
4	45	350	A	2.2	1.4	1.07	73.5	
7	45	350	A	2.3	1.1	0.83	75.2	Lummus 3LCF7 pasting solvent composite used as solvent
10	45	375	A	2.3	1.1	0.82	83.5	
14	60	350	A	1.4	2.2	1.68	83.7	Sample filtered, THF-sols distilled to remove solvent
15	45	400	A	2.3	0.0	0.00	70.0	
16	60	350	A	1.4	1.9	1.50	84.4	Sample filtered, THF-sols distilled to remove solvent
17	60	375	A	2.2	1.4	1.04	89.5	"
18	45	400	A	2.2	1.4	1.05	92.1	"
19	60	350	A	1.4	2.2	1.71	83.7	
42a	60	353	A	2.2	2.2	0.80	80.9	
42b	60	350	A	2.2	2.2	0.81	79.5	
43b	60	350	A	2.2	2.2	0.50	70.8	
43c	45	350	A	2.2	2.2	1.64	76.7	
49	0*	200-350	A	2.2	1.1	0.83	33.8	Heating rate ~5 °C/min to 350 °C
50	30*	200-350	A	2.2	1.1	0.92	58.9	"
55	120	350	A	2.2	1.1	0.84	80.2	
56	60	200-350	A	2.2	1.1	0.87	78.8	Heating rate ~2 °C/min to 350 °C
60	15-	385	A	2.2	1.1	0.88	94.0	

*Residence time at temperature

TABLE 2

MICROAUTOCLAVE TEST CONDITIONS AND RESULTS
Black Thunder Mine, Wyoming Subbituminous Coal

Run No.	Time, Min	Temp, °C	Hydride Ion Reagent	Solvent: dry coal g:g	HI:dry Coal g:g	HI:H_2O mole Ratio	Coal Conversion wt % MAF coal, SO_3-free Basis	Comments
20	45	400	A	2.0	1.0	1.33	87.5	
21	45	375	A	2.0	1.0	1.13	80.0	
22	45	350	A	2.0	1.0	1.17	62.9	
23	30	400	A	2.0	1.0	1.30	86.7	
24	60	400	A	2.0	1.0	1.18	86.7	
25	45	400	A	2.0	1.3	1.44	88.2	
26	45	400	A	2.0	1.5	1.77	90.0	
27	45	400	A	2.0	1.8	2.03	89.9	
28	45	400	A	2.0	2.0	2.26	90.7	
30	45	400	A	2.0	3.2	3.49	90.6	
31	45	400	B	2.0	1.0	1.20	70.7	Conversion based on water-washed THF insolubles
32	45	350	B	1.9	1.0	1.27	72.3	Conversion based on water-washed THF insolubles
33	45	350	B	2.0	1.7	2.06	17.3**	Conversion based on water-washed THF insolubles
34	45	400	A	2.2	1.7	1.24	90.2	
35	45	400	A	2.7	2.0	0.87	91.3	
36	45	350	A	2.0	3.2	3.47	81.1	
37	45	350	A	4.4	6.9	1.17	88.4	
38c	45	350	A	1.9	2.4	3.30	76.3	
39	45	350	A	2.0	0.0	0.00	36.5	
40	45	375	A	2.0	0.0	0.00	50.5	
41	45	400	A	2.0	0.0	0.00	69.9	
44	45	350	A	2.1	2.1	0.77	80.1	
45	45	350	A	2.1	1.0	0.74	65.5	
46	45	350	A	2.6	3.2	0.80	79.7	
47	15	350	A	2.0	1.0	1.10	46.3	
48	90	350	A	2.0	1.0	1.10	75.2	
51	0*	200-350	A	2.0	1.07	1.29	45.7	Heating rate ~3 °C/min to 350 °C
54	120	350	A	2.0	1.0	1.10	71.7	
57	45*	200-350	A	2.0	1.0	1.11	66.4	Heating rate ~4 °C/min to 350 °C
58	90	375	A	2.1	1.0	1.08	88.2	
59	120	375	A	2.1	1.0	1.06	89.5	

*Residence Time at temperature; **Suspect

TABLE 3

RESULTS FROM THE CATALYST ACTIVATION STUDY IN THE CAER MICROAUTOCLAVE

Run No.	Catalyst Used/ Concentration	Pretreat-ment Step[a]	H_2 Consumed, mg/g MAF Resid	Hydrocarbon Gas Yield, wt % MAF Resid	Resid Conversion, wt % MAF Resid
R5-290-1	none	no	7	6.2	19
R5-292-1	Molyvan L/ hexadecane (1000 ppm Mo)	no	18	5.8	35
R5-320-2		yes	18	6.2	36
R5-320-1	ex situ presulfided AO60 (1000 ppm Mo+Ni)	no	16	5.7	38
R5-314-1	As-received AO60	no	19	9.5	36
R5-318-1		yes	20	9.4	48
R5-307-2	Mo naphthenate/ hexadecane (1000 ppm Mo)	no	17	9.4	37
R5-318-2		yes	16	6.0	36

a. Pretreatment at 375 °C for 30 minutes.

DISCLAIMER